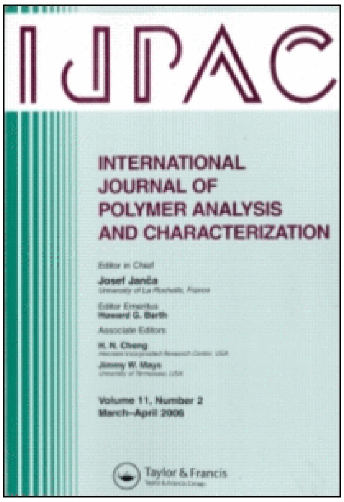

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Ramalingam, Periasamy , Smith, O'Neil and Seo, Seong S.(2009) 'Monitoring of Colloidal Crystal Formation of Highly Charged Polystyrene and pH Sensing', International Journal of Polymer Analysis and Characterization, 14: 4, 291 — 300

To link to this Article: DOI: 10.1080/10236660902866793

URL: http://dx.doi.org/10.1080/10236660902866793

International Journal of Polymer Anal. Charact., 14: 291–300, 2009
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ISSN 1023-666X print
DOI: 10.1080/10236660902866793

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Monitoring of Colloidal Crystal Formation of Highly Charged Polystyrene and pH Sensing

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Abstract: Colloidal crystals have been given a lot of attention in the scientific arena because of their versatility. Here we present a drop and slide technique that was adopted to fabricate a 3-D colloidal crystal array from an aqueous solution of monodispersed, highly charged polystyrene spheres. Bragg reflectance spectra were obtained for the array of colloidal crystal at 50% volume fraction of the colloids as a function of time. The time-resolved Bragg reflection spectra observed show a reflection peak maximum gradually moving towards higher energy state during the colloidal crystallization process. The path taken as the wavelength blue-shifts during drying has been hypothesized to be highly dependent on not only the ordering, but also the shape of the liquid-air interface. The study also highlights the crystallization process during drying. The pH effect on reflectance spectra was also studied on the crystal array by introducing various pH solutions into the system. The results of the pH investigation show that the reflectance spectra are blue-shifted as the pH decreases.

Keywords: Bragg diffraction; Charged colloidal crystal array; Highly charged polystyrene, pH sensing; Reflectance spectroscopy

Submitted 5 January 2009; accepted 22 January 2009.

This work was supported by grants from the National Institutes of Health, RIMI program, Grant P20 MD001085, and the Department of Defense, Grant W911NF-06-1-0433, whose support is greatly appreciated.

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INTRODUCTION

Charged colloidal particles dispersed in aqueous media are stabilized due to long-range electrostatic interparticle interactions.[1–3] When the interaction forces are weak, their spatial distributions are highly disordered. With increasing interaction, the charged colloids undergo a phase transition to the ordered "crystal" state, where the particles are regularly arranged. The crystallizations of charged colloids have been studied extensively as they have attracted considerable attention as photonic crystals since their Bragg reflection wavelengths usually lie in the optical region.[1–6] Research efforts have been directed towards the use of colloidal crystals in the area of photonics owing to the periodic structures of these materials. These materials may find uses in chemical sensors, optical switches, and optical filters. In addition, monodisperse colloidal particles undergo entropically driven phase transitions as a function of particle volume fraction (φ). Asher and coworkers[5,6] fabricated hydrogel-containing highly charged monodispersed particles that changed color depending on their external environment such as temperature and metal ion concentration.

There are several factors that govern the formation and orientation of colloidal crystals, such as the size, surface charge, and ionic strength of the medium.[5,6] The crystals are generally face-centered cubic (FCC) at high volume fractions with low surface charges and body-centered cubic (BCC) at low volume fractions with high surface charges.[4,7–9] The lattice spacing in these systems usually exceed 100 nm, hence the dispersion efficiently diffracts visible light according to the Bragg diffraction equation[10] $\mathbf{n}\lambda = 2n_{eff} d \sin\theta$, where λ is the wavelength of diffracted light, **n** is the order of diffraction, d is the inter-planar spacing, n_{eff} is the effective refractive index of the dispersion, and θ is the Bragg angle. It has been shown that diffraction wavelengths from liquid colloidal dispersions can be tuned by varying the particle size, particle concentration, and Bragg angle.[11–13] It is this tunable characteristic of these crystal lattices as depicted by Bragg's law that has brought about the rapid progress towards their usage in optical devices.

The first aim of this article is to reveal the colloidal crystallization process of highly charged polystyrene by monitoring the time-resolved reflection spectra. The second aim is to study the behavior of highly charged polystyrene colloidal crystal array (CCA) films in various pH solutions to gain insight into the tuning of the diffraction wavelength by the manipulation of surface charges and ionic strength of the solvent. It is our hypothesis that the addition of a small quantity of acidic solution changes the surface charge of the CCA and causes the inter-spacing to vary and thereby alter the Bragg diffraction.

EXPERIMENTAL SECTION

Materials/Procedures

For the preparation of the CCA, we obtained OptiBind polystyrene microparticles (PS-MPs; Seradyn Inc, Ind., USA), which are uniformly sized (0.210 μm) stable colloids and are considered to be monodispersed spheres. The density of polystyrene is 1.05 g/mL and the carboxyl content is 0.210 meq/g. Polystyrene colloidal spheres were centrifuged seven times. The final product is an iridescent opal-colored colloidal microgel. The gel mainly reflects light in the green to red region. The particles are supplied at nominal 10% solids after dilution with distilled water from the original polymerization mixture. The stability of the colloids (i.e., maintaining spheres as separate particles) requires a minimum amount of surface negative charge. The slide and cover glasses (Fisher) used for creating a uniform thin layer of the colloids were first treated with freshly prepared piranha solution (H_2SO_4/H_2O_2, ratio of 3:1). The glass substrates were rinsed copiously with distilled water and subsequently dried under the flow of N_2. Such chemical modification of the substrate surfaces is known as an effective way to facilitate the preparation of laterally patterned colloidal crystals.[14]

Drop-Slide Method to Form a CCA

An easy drop and slide technique was used to form the CCA as shown in Figure 1.[15–17] Micro droplets of the aqueous colloidal spheres were first placed on a glass slide and spread manually using a cover glass slide. For the pH studies, small amounts of 2 M HCl solution were added on the droplets of the aqueous colloidal spheres. As soon as the particles come in contact with the cover glass they are spread along the long edge of the cover glass manually. The cover glass is then very slowly tipped right along the length of the glass slide causing the colloidal particles to thinly and uniformly spread on the substrate. Although this method provides a relatively easy route to create uniformly spread crystal lattice, it has no

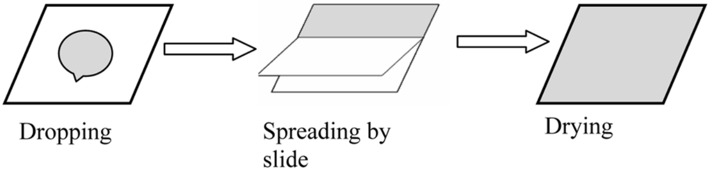

Figure 1. Schematic diagram of the new drop slide procedures.[17]

provisions for the control of thickness based on sliding speed and hence has room for improvement. This method is similar to that used by Ko and Shin,[18] however here we used a pipette to deposit the particles horizontally on the substrate and then spread them with a cover slip. The self-assembly of the CCA from the wet to the dry state was monitored by taking reflection spectra at normal incidence using an Ocean Optics USB 2000 fiber optic spectrometer. Usually, the high optical quality of the film can be judged by the naked eye due to the opalescence. The reflection spectra were obtained in the region from 350 to 1000 nm. The reflection spectra were obtained over selected time intervals (2 and 4 min) from the placement of the colloidal particles on the substrate until the dry state was attained, as indicated both visibly and by a strong Bragg reflection in the visible region. In order to determine morphology of the films, scanning electron microscopy (SEM, JSM-5900) was used.

RESULTS AND DISCUSSIONS

Figure 2 shows a scanning electron microscope image of the colloidal particles. Cracks were evident in the film, which were induced by the shrinkage of the particles as the solvent evaporated. Figure 2 demonstrates that the particles undergo self-assembly into a regular CCA. Upon drying, the highly ordered array was seen to have a face-centered cubic (FCC) crystal structure that is consistent with the (111) miller indices. The Bragg reflectance spectrum for highly charged polystyrene colloids with volume fraction of $\varphi = 0.74$ is shown in Figure 3. The spectrum was obtained 2 min after placing the colloid film on the glass substrate. The spectrum indicates

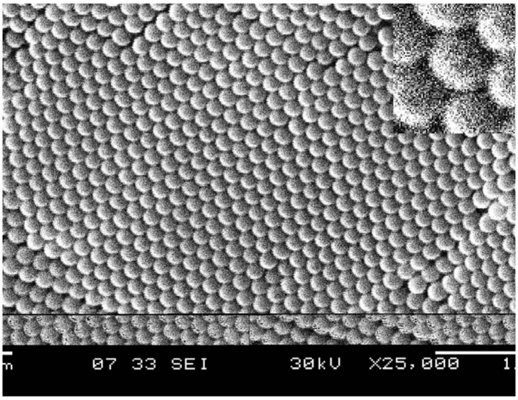

Figure 2. Scanning electron microscope image of highly charged polystyrene colloids with a high resolution image.

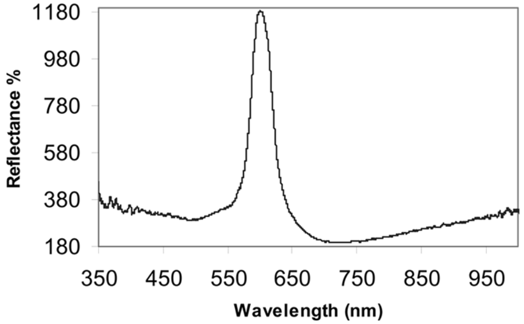

Figure 3. Bragg reflectance spectrum for highly charged polystyrene colloids.

that the self-assembly of the particles into a CCA was almost instantaneous based on the relatively strong Bragg reflectance obtained after 2 min. The reflection maximum at $\lambda = 601.5$ nm is highly symmetrical and has a narrow line width of ~50 nm. The symmetry is indicative of the uniformity of the crystal arrangement throughout the lattice. In situ Bragg reflectance spectroscopy was used to analyze the crystallization process of the colloidal film, as has been done by Koh's group.[2]

Figure 4 shows the variations in the Bragg reflectance peak maximum observed in situ starting from about 2 min after the colloid is allowed to set on the substrate. The time interval between scans was 5 min, and each spectrum was averaged over two scans. Although the figure shows reflectance for up to the 35 min mark, it must be noted that under ambient conditions, the films required 45–60 min to become completely dry.

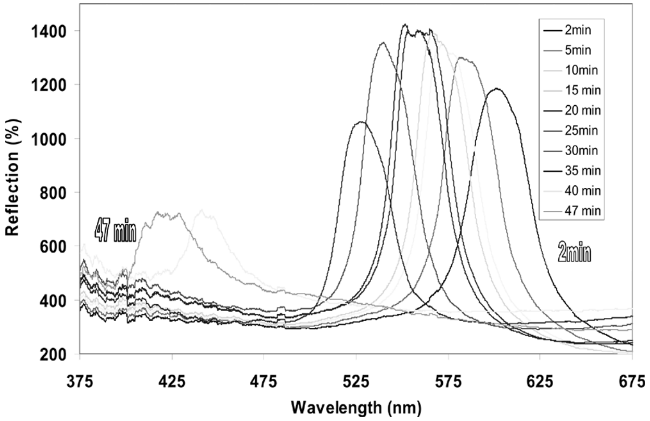

Figure 4. Time-resolved Bragg reflectance maximum for highly charged polystyrene CCA.

It was observed that the colloidal particles that were set on the cover glass slide exhibit a gradually increasing opal iridescent, and upon illumination under the incident light, the top surface seems to reflect a strong greenish and red light. This phenomenon may be attributed to the steady formation of a more ordered structure as time progresses, which as mentioned before, may be correlated to the uniformity of the lattice. The entropically driven ordering of the crystals, as exhibited in the reflection spectra, is dependent on the rate of evaporation of water.[2] Initially when the film is placed on the glass substrate, there is no evidence of any drastic change in the crystal structure (as indicated by the spectra) of the array, since at this stage, the arrangement of the particles is solely dependent on the inter-repulsive forces between the negatively charged particles.[1,7–9] As the sample dries, the initial diffraction peak observed at 601.5 nm blue-shifts to 424 nm after the 47 min mark. The arrangement of the CCA at the 47 min mark is thought to be indicative of the final dry state since after this point there was no significant observable change in the diffraction maximum. Details of this will be further highlighted in Figure 5. This gradual blue-shift can be ascribed to the shrinkage in the colloidal film as the solvent evaporates. The evaporation causes the film to shrink and in effect causes the inter-lattice spacing to become smaller. In addition to the reduction in the inter-lattice spacing, there is a consequent increase in the density of the lattice that parallels an increase in its effective refractive index.[19] In Figure 3, the intensity of the reflection maximum shows an initial gradual increase followed by a subsequent steady decrease. The reflection spectra obtained from the colloidal film as it transitions from its wet state to the dry state show maximum peak intensity at the 25 min mark, after which the intensity

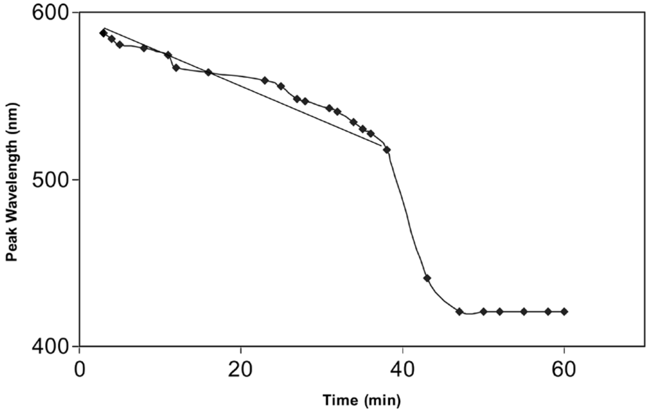

Figure 5. Time-resolved Bragg reflection maximum of highly charged polystyrene for the drying process.

steadily decreases. At this point, the CCA may be considered to have reached a point where there is a greater balance between the inter-repulsive forces.[6]

Figure 5 shows a plot of the peak values of the Bragg reflection maximum versus time. For the first 38 min, the peak wavelength gradually shifts at a rate of 2.0 nm/min. The decrease in the peak wavelength indicates the lattice parameter of the FCC structure is shrinking over time. In contrast, the peak wavelength sharply decreased at a rate of 11.8 nm/min between 38 and 47 min. This sharp reduction in rate indicates that there is a decrease in the lattice parameters towards the end of the crystallization process during drying. The reflection maximum initially has a close to linear behavior, suggesting that the monodisperse colloidal particles, which have covalently attached ionizing groups, will self-assemble in solution into a highly ordered, non-close-packed three-dimensional array. As the solvent evaporates, thereby reducing or eliminating the counter-ion effect that is needed for the surfaces of colloidal particles, a sudden drop is seen in the wavelength for consecutive time intervals.[2] This behavior can be compared with the results of the crystallization process of very low charged polystyrene (carboxyl content $= 0.061$ meq/g) CCA.[15–17] A near linear blue-shift in the peak position was observed on the low charged CCA film for the first drying phase with a rate of 4.1 nm/min, while the peak shifts are exponentially dependent on time for the second drying phase. As mentioned before, at and beyond the 47 min mark there is no significant change in the diffraction wavelength. This observation is amplified in Figure 5 and serves to validate that this point is reflective of the dry state for the CCA.

The time-resolved variation of the inter-lattice spacing of a crystal array has been attributed to the changes in surface negative charges that the colloids possess, and hence it can be utilized to see if such a change in the charge can be determined by reflection spectroscopy. Some of the negative charges of the functional groups of the highly charged polystyrene can be neutralized by the addition of small quantities of 2 M HCl. We propose that the diffraction from a CCA composed of highly charged polystyrene can be used to sense pH and ionic strength of a solvent. It can be seen in Figure 4 that the peaks around the 20 and 25 min marks have distinct plateaus that we believe to be inherent in the ordering of the CCAs. Although the rationale for this anomaly still remains elusive, we hypothesize that the observed plateau is indicative of a transition point between two lattice crystal structures (i.e., face-centered-cubic (FCC) and body-centered-cubic (BCC)). It is known that colloidal particles, in an effort to minimize interparticle repulsion, will tend to adopt either FCC or BCC lattice structures.[20] Figure 2 shows that in the dry state (beyond 47 min), our CCAs have an FCC arrangement. Additionally, it has been shown that the BCC structure is preferred at low volume fractions, while the FCC structure is favored at high volume fractions.[4,7–9] This lends to the idea that the peak maxima with the plateaus not only signify a balance of charge as stated earlier, but also a transition point from a BCC to an FCC lattice structure. However, in order to conclusively prove this, further tests must be conducted.

Figure 6 shows the behavior of the reflection maximum as equal volumes of various pH solutions were added to a fixed quantity of CCA. Here the total volume fraction is kept constant so as to better elucidate the pH effects of the system. In addition, different pH values of HCl solutions were added to the colloidal suspension. The spectra were obtained 4 min after the placement of the colloid on the cover glass. At normal incidence, CCA in deionized water is at a pH of 6.8 and diffracts light at 628.4 nm. For pH 5.4 the diffraction maximum was observed to be at 561.0 nm. The peak maximum was observed to be monotonically blue-shifting up to 424.2 nm for pH of 5.2. The diffraction peaks remain symmetric for all the observed pH strengths, which indicate preservation of ordering of the CCA. Here a reduction in pH is consistent with the increased protonation of the terminal carboxyl groups on the PS particles. The neutralization of these particles minimizes the repulsive force between the particles, allowing them to come within closer proximity to each other, thereby, decreasing the refractive index. It is this denser, ordered structure that accounts in the gradual blue-shifting in the diffraction peak. The pH dependence shown in Figure 6 may be used to develop a model sensor for pH determinations using polystyrene CCA.

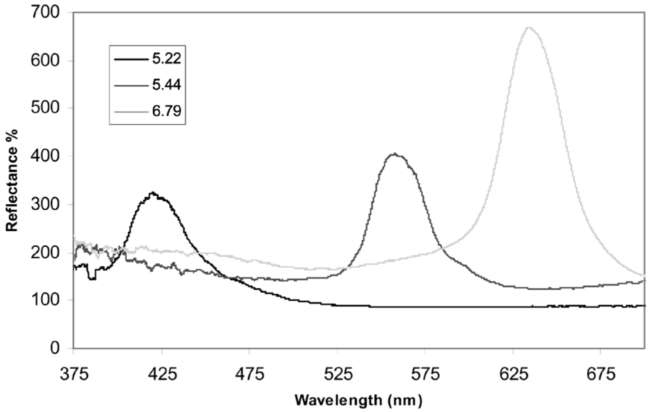

Figure 6. Behavior of highly charged polystyrene crystal colloidal array with changes in pH.

CONCLUSION

In this article we have shown a drop-and-slide method for the preparation of colloidal crystal arrays on a horizontal surface. The method is designed to yield a more uniform self-assembly layer on the chosen substrate. In situ reflectance studies revealed the crystallization process of the colloidal system. The carboxyl-terminated colloids used in this study have been shown to give characteristic reflectance based on pH. These results indicate that these particles may be useful in the design of devices for determining pH.

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